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(54) PRODUCTION OF FLAMEPROOF POLYURETHANE FOAM RESINS

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SCHAFT, formerly known as Farbenfabriken
Bayer Aktiengesellschaft, a body corporate
organised under the laws of Germany of 509
Leverkusen, Germany, do hereby declare the
invention, for which we pray that a patent
may be granted to us, and the method by
which it is to be performed, to be particu-
larly described in and by the following state-
ment:—

This invention relates to a process for the
production of polyurethane foams, which are
flameproof. This invention is a modification
of or an improvement in the invention des-
cribed in our patent application No. 1,267,011
(herein termed the Main Patent).

The Main Patent relates to a process for
the production of a polyurethane foam which
comprises reacting:

- (a) at least one polyether which contains
at least 2 reactive hydrogen atoms and
has a molecular weight of 1,500 to
10,000 and in which at least 10% of
the hydroxyl groups present are prim-
ary hydroxyl groups,
(b) at least one polyisocyanate solution
which is a solution of at least one poly-
isocyanate which contains at least one
isocyanuric acid ring dissolved in a
monomeric polyisocyanate which is free
from isocyanurate groups, and
(c) a blowing agent.

In the course of further development on
the process of the Main Patent it has now
been found that flame-proof polyurethane
foams can also be produced with unexpectedly
advantageous properties if, instead of using
the polyisocyanates specified in the Main
Patent, there are used 1 to 80% by weight
solutions (preferably 5 to 60% by weight

solutions) of polyisocyanates which contain at
least one isocyanuric acid ring, (i.e. isocyan-
urate group) and, if desired, additional
urethane groups in polyisocyanate which con-
tain urethane groups and which are free from
isocyanurate groups. If desired, monomeric
isocyanates which contain neither isocyan-
urate groups nor urethane groups, may be
added as solvents.

The reactants used for the production of
the foam resins are otherwise the same as
those used in the Main Patent. Accord-
ingly the invention provides a process for the
production of a polyurethane foam which
comprises reacting:—

- (a) at least one polyether which contains
at least two reactive hydrogen atoms and
has a molecular weight of 1,500 to
10,000 and in which at least 10% of
the hydroxyl groups are primary
hydroxyl groups.
(b) at least one polyisocyanate solution
which is a 1 to 80% solution by weight
of at least one polyisocyanate which com-
prises at least one isocyanurate ring dis-
solved in at least one polyisocyanate which
is free from isocyanurate groups but
which comprises urethane groups.
(c) a blowing agent.

The polyisocyanates which contain iso-
cyanurate groups and also, if desired, urethane
groups may be those polyisocyanates given
in the Main Patent which contain at least
one isocyanuric acid ring.

In many cases, however, it is desirable to
react these polyisocyanates with less than
equivalent quantities of compounds of mole-
cular weight 31 to 10,000 which contain
hydroxyl groups additional urethane groups
thus being introduced into the polyisocyanate

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component. This enables the storage stability of the polyisocyanate used according to the invention to be improved.

The polyisocyanates used according to the invention which are employed in the form of the specified solutions, therefore contain at least one isocyanuric acid ring and, if desired, additional urethane groups. The introduction of the urethane groups may be effected before and/or after formation of the isocyanuric acid ring.

The compounds of molecular weight 31 to 10,000 which contain hydroxyl groups may be monofunctional, bifunctional, trifunctional, and higher functional hydroxyl compounds of conventional type. Methanol, butanol, oleyl alcohol and stearyl alcohol are given as examples of monofunctional hydroxyl compounds. It is preferred, however, to use bifunctional to octafunctional hydroxyl compounds, e.g. ethylene glycol, trimethylolpropane, pentaerythritol, sorbitol polyesters, and polyethers which contain hydroxyl groups, e.g. also polyethers which are obtained by the reaction of ethylene oxide and/or propylene oxide in the presence of polyfunctional initiator molecules such as water, alcohols or amines, including sucrose. The hydroxyl compounds preferably have a molecular weight of from 60 to 5000.

The solvents used for the polyisocyanate which contains at least one isocyanuric acid ring and, if desired, also urethane groups may be, as already mentioned above, the polyisocyanates already mentioned in the Main Patent which are free from isocyanurate groups and contain urethane groups and also, if desired, those monomeric polyisocyanates which are free from isocyanurate groups and from urethane groups.

The polyisocyanates which are free from isocyanurate groups and contain urethane groups may be prepared from conventional aliphatic, cycloaliphatic, araliphatic and aromatic polyisocyanates, e.g. hexamethylene diisocyanate, cyclohexane - 1,3 - and 1,4 - diisocyanate, tolylene - 2,4 - and/or - 2,6 - diisocyanate, 4,4' - diphenylmethanediisocyanate and m- and p-xylylene diisocyanate.

The following compounds are given as examples of polyhydroxyl compounds which may be used with the polyisocyanates for the preparation of the polyisocyanates which are free from isocyanurate groups and which contain urethane groups: butane - 1,3 - diol, butane - 1,4 - diol, diethyleneglycol, triethyleneglycol, propane - 1,2 - diol, dipropylene glycol, tripropyleneglycol, 2,3-dimethylpentanediol, 2,2 - dimethylpropane - 1,3 - diol, pentane - 1,5 - diol, hexane - 2,5 - diol, 3 - methyl - pentane - 2,4 - diol, 2,2' - dihydroxydiethylsulphide, octadecane - 1,2 - diol, octaethyleneglycol, 4,4' - dihydroxy - dicyclohexyl - dimethylmethane, 1,5 - dihydroxy - decahydronaphthalene, 1,4 -

dihydroxy - cyclohexane, hydroquinone, resorcinol, 4,4' - dihydroxydiphenyl - dimethylmethane, 4,4' - dihydroxydiphenyl - carbonate, 2,2' - dihydroxy - diphenyl, 4,4' - dihydroxy - octachlorodiphenyl - dimethylmethane, 1,5 - dihydroxy - naphthalene, glycerol, trimethylolpropane, hexanetriol, polyphenols according to U.S. Patent Specification No. 3,330,781, phloro-glucinol, pyrogallol, oxyhydroquinone; trihydroxytriphenylmethanes and their perhydrogenated analogues, pentaerythritol, sorbitol, mannitol, dulcitol, tetrosene, pentose, hexosene, disaccharides such as sucrose or cellulose, reaction products of polyhydric alcohols with at least one mol of an alkylene oxide such as ethylene oxide, propylene oxide, butylene oxide or styrene oxide, glycidol or mixtures of such epoxides to produce hydroxyl containing polyethers with hydroxyl numbers of 28 to 1500. The hydroxyl containing components for the reaction with polyisocyanates to produce urethane containing polyisocyanates may also be phenol formaldehyde condensation products, e.g. those prepared from phenol and formaldehyde in a molar ratio of 1:0.8, or polyesterpolyols with hydroxyl numbers of 35 to 650 prepared from linear and/or branched polyhydric alcohols. These compounds also include naturally occurring plant oils which contain free hydroxyl groups, e.g. castor oil.

Urethane containing polyols obtained from the above mentioned hydroxyl compounds and aliphatic, aromatic and/or araliphatic polyisocyanates may also be used as components for the preparation of the polyisocyanates which contain urethane groups.

Hydroxyalkylphosphorous acid esters or hydroxyalkylphosphoric acid esters may also advantageously be used.

The following are examples of suitable polyols which contain amide groups: Acid amides of diethanolamine or diisopropanolamine and aliphatic or aromatic dicarboxylic acids or hydroxycarboxylic acid such as glycolic acid, lactic acid, salicylic acid, p-hydroxybenzoic acid and hydroxyalkylbenzene carboxylic acids. The polyols which contain amide groups may also be prepared by reacting acid amides or low molecular weight polyamides with epoxides such as ethylene oxide, propylene oxide, butylene oxide, styrene oxide or mixtures thereof. Epoxide addition products with ammonia, substituted or unsubstituted hydrazines, primary aliphatic, cycloaliphatic, aromatic or araliphatic amines may also be used according to the invention.

Polyols suitable for use according to the invention may also be prepared by reacting diethanolamine, diisopropanolamine and other open chain or cyclic hydroxyalkylamines which have NH groups with ethylene glycol

carbonate to produce polyfunctional hydroxy-alkylurethanes.

5 Mannich condensation products of CH acidic compounds, alkylphosphorus acid esters, formaldehyde and secondary amines which contain hydroxyl groups may also be used.

10 The polyisocyanates which contain urethane groups are prepared by reacting the reactants at an NCO/OH ratio greater than 1 and then optionally dissolving the reaction product in monomeric diisocyanate to obtain the required concentration.

15 The prepolymer (polyisocyanate containing urethane groups) may subsequently be dissolved in the same polyisocyanate which was used for preparing it although it may also be advantageous to prepare the prepolymer with a less reactive polyisocyanate, e.g. an aliphatic, cycloaliphatic or araliphatic diisocyanate, and then to dissolve it in an aromatic diisocyanate. The reactive isocyanate groups present in such a polyisocyanate which contains urethane groups are highly differentiated in their reactivity, and the structure of the high molecular weight polyurethane can be additionally influenced at the stage of foaming by suitable choice of these isocyanate groups if control of the foaming process by means of catalysts and/or additives alone is not sufficient.

20 The polyisocyanate solutions which contain urethane groups may also be prepared in a single stage operation by reacting the polyols with excess polyisocyanates; the prepolymers can be adjusted to any desired concentration in this process.

25 The foam resin produced according to the invention have a higher bond strength on textiles and non-textile substrates when applied by flame backing.

30 The foam resin produced according to the invention also have an improved response to high frequency welding.

35 The foam resins produced by the process according to the invention can be used, for example, as upholstery material, mattresses, packaging material, shock absorbing motor car parts, foils for backing or for high frequency welding and insulating materials. The parts used may either be produced by foaming in the mould or they may be manufactured from material which has been foamed in the block.

40 In the course of our development work on the process of the Main Patent, we have also found another modification or improvement in which component (b) is a 1 to

80% by weight solution of one or more polyisocyanates which contain at least one isocyanurate group and which have been reacted with a less than equivalent amount of at least one hydroxyl containing compound having a molecular weight of 31 to 10,000 the solution being in at least one monomeric polyisocyanate free from isocyanurate groups. This is described and claimed in our copending application No. 49600/71, (Serial No. 1337660).

The invention is illustrated by the following Examples.

Example 1

100 Parts by weight of polypropylene glycol (component (a)) which has been initiated on trimethylolpropane and tipped with ethylene oxide to produce approximately 72% of primary hydroxyl groups in end positions with an OH number of 38.1,

0.3 parts by weight of triethylene diamine, 2.5 parts by weight of water (blowing agent) and

53 parts by weight of a polyisocyanate solution (component b)) which consists of 95% of an isocyanate which contains urethane groups and 5% of a polymeric tolylene - 2,4 - diisocyanate which contains isocyanurate groups (NCO content 21.1%) are reacted together. The isocyanate which contains urethane groups was prepared as follows:

79 Parts by weight of a mixture of 70% by weight of trimethylolpropane and 30% by weight of butane - 1,3 - diol are reacted with 921 parts by weight of an isomeric tolylene diisocyanate mixture (65% of 2,4 - diisocyanatotoluene and 35% of 2,6 - diisocyanatotoluene) at 80 to 100°C and unreacted diisocyanate is then removed by distillation to yield a polyurethane which contains approximately 17% by weight of NCO groups. 40% by weight of this product, which is in the form of a solid resin, are dissolved in 60 parts by weight of an isomeric tolylene diisocyanate mixture (80% 2,4- and 20% 2,6-isomer); the clear solution obtained has an NCO content of 35.5% and a viscosity of 140 cP at 25°C.

The above mentioned components were mixed together. Foam formation begins after an induction period of 10 seconds and is completed after an expanding time of 75 seconds. The highly elastic foam resin obtained has the following properties:

	Density according to DIN 53420	40 kg/m ³
	Tensile strength according to DIN 53571	0.9 kg wt/cm ²
5	Elongation at break according to DIN 53571	180%
	Compression strength at 40% compression according to DIN 53577	27 p/cm ²
	Flammability test according to ASTM D 1692/67 T	3.0
10	Average length of burnt sample (cm)	16
	Average extinction time (sec)	16

The foam resin is therefore to be regarded as self-extinguishing.

Example 2

- 15 100 Parts by weight of a polypropylene glycol which has been initiated on trimethylolpropane and tipped with ethylene oxide to produce approximately 72% of primary hydroxyl groups in end positions with an OH number of 38.1, 20 0.3 parts by weight of triethylene diamine, 2.5 parts by weight of water and 48 parts by weight of an isocyanate mixture which consists of 95% of an isocyanate which contains urethane groups (see A—below) and 5% of a 2,4- and 2,6-tolylene diisocyanate containing urethane groups and isocyanurate groups (see B—below) (NCO content 38.9%) 25 are reacted together. The isocyanate which contains urethane groups was prepared as follows:

- A.—A polyurethane which contains approximately 17% by weight of NCO groups is prepared by reacting 79 parts by weight of a mixture of 70% by weight of trimethylol propane and 30% by weight of butane - 1,3 - diol with 921 parts by weight of an isomeric tolylene diisocyanate mixture (65% of 2,4 - diisocyanatotoluene and 35% of 2,6 - diisocyanatotoluene) at 80 to 100°C. and then removing the unreacted diisocyanate by distillation. 40 Parts by weight of this product which is in the form of a solid resin are dissolved in 60 parts by weight of an isomeric tolylene diisocyanate mixture (80% 2,4- and 20% 2,6-

isomer). The clear solution obtained has an NCO content of 35.5% and a viscosity of 140 cP at 25°C. The polyisocyanate which contains isocyanurate groups was prepared as follows:

- B.—1.96 Parts by weight of 1,2-propylene glycol are added to 35 parts by weight of an 80:20 percent by weight isomeric mixture of 2,4- and 2,6-tolylene diisocyanate at 60°C and the compounds are left to react together for 30 minutes during which time the reaction mixture heats up to 80°C. After the addition of 0.037 parts by weight of β -phenylethyl-ethyleneimine, the reaction mixture is heated to 130°C and it is left at this temperature, at which it undergoes trimerisation to form isocyanurate groups, until an NCO value of 30% is reached, which requires about 1 to 2 hours. After cooling to 100°C. 3.7 parts by weight of tripropylene glycol are added and the reaction is left to proceed for one hour at the same temperature. The reaction mixture, which has an NCO value of 23.3% at the end of this time, is then diluted with 65.06 parts by weight of an 80/20 mixture of 2,4- and 2,6-tolylene diisocyanate. The polyisocyanate solution obtained has the following properties:

% NCO=38.9, $cP_{25°C.}=39$, $n_D^{50}=1.5642$ 80

A foam resin which has the following mechanical properties is obtained:

	Density DIN 53420	(kg/m ³)	40
	Tensile strength according to DIN 53571	(kg wt/cm ²)	0.8
85	Elongation at break according to DIN 53571	(%)	130
	Compression test DIN 53577	(p/cm ²)	30
	Inflammability according to ASTM D 1692—67T		
90	Average length of burnt sample (cm)		3.5
	Average extinction time (sec)		18
	Assessment		self-extinguishing

Example 3

100 Parts by weight of a polypropylene glycol which has been initiated on trimethylolpropane and tipped with ethylene oxide to produce approximately 72% of primary hydroxyl groups in end positions with an OH number of 38.1, 0.3 parts by weight of triethylenediamine, 2.5 parts by weight of water, and 48 parts by weight of an isocyanate mixture which consists of 95% of isocyanate which contains urethane groups and 5% of a 2,4- and 2,6-tolylene diisocyanate mixture which contains urethane groups and isocyanurate groups (NCO content 39.0%) are reacted together.

The urethane isocyanate was prepared as given in Example 2-A.

The polyisocyanate which contains isocyanurate groups was prepared using the same method as in Example 2B but adding 2.03 parts of trimethylol propane instead of tripropylene glycol and diluting the reaction mixture with 66.30 parts of an 80/20 mixture of 2,4- and 2,6-tolylene diisocyanate. This yielded a polyisocyanate solution which has the following properties:

$$\% \text{NCO} = 39.0, \text{cP}_{25\text{deg.}} = 58, n_D^{50} = 1.5682.$$

A foam resin which has the following mechanical properties is obtained:

Density DIN 53420	(kg/m ³)	40
Tensile strength according to DIN 53571	(kg/wt/cm ²)	1.0
Elongation at break according to DIN 53571	(%)	150
Compression test DIN 53577	(p/cm ²)	30
Inflammability according to ASTM D 1692—67 T		
Average length of burnt sample (cm)		3.8
Average extinction time (sec)		22
Assessment		self-extinguishing

Example 4

100 Parts by weight of a polypropylene glycol which has been initiated on trimethylolpropane and tipped with ethylene oxide to produce approximately 72% of primary hydroxyl groups in end position with an OH number of 38.1, 0.3 Parts by weight of triethylenediamine, 2.5 parts by weight of water, and 46 parts by weight of an isocyanate mixture which consists of 95% of an isocyanate which contains urethane groups and 5% of a 2,4-tolylene diisocyanate (NCO content 39.4%) which contains urethane groups and isocyanurate groups are reacted together.

The isocyanate which contains urethane groups was prepared as in Example 2-A.

The polyisocyanate which contains isocyanurate groups was prepared as follows:

B.—1.54 Parts of 1,2-propylene glycol are added to 38.46 parts of tolylene - 2,4 - diisocyanate at 60°C in a vessel equipped with a stirrer under nitrogen (used as

protective gas), and the reactants are left to react together for 30 minutes, during which time the mixture heats up to 95 to 100°C without external supply of heat. After the addition of 0.060 of β - phenylethyl - ethyleneimine, the reaction mixture is heated to 130°C and left at this temperature until, after about 5 to 6 hours, the NCO content is 26.0%. Trimerisation of the polyisocyanate is then stopped by the addition of 0.038 parts of methyl p-toluenesulphonate, and the reaction mixture is diluted with 60.00 parts of an 80/20 mixture of 2,4- and 2,6-tolylene diisocyanate after it has been cooled to 120°C. The reaction mixture is characterised by the following properties:

$$\% \text{NCO} = 39.4, \text{cP}_{25\text{deg.}} = 63, n_D^{50} = 1.5721.$$

A foam resin which has the following mechanical properties is obtained:

Density DIN 53420	(kg/m ³)	41
Tensile strength according to DIN 53571	(kg wt/cm ²)	1.0
Elongation at break according to DIN 53571	(%)	160
Compression test DIN 53577	(p/cm ²)	28
Inflammability according to ASTM D 1692—67 T		
Average length of burnt sample	(cm)	3.3
Average extinction time	(sec)	27
Assessment		self-extinguishing

Example 5

100 Parts by weight of a polypropylene glycol which has been initiated on trimethylol propane and tipped with ethylene oxide to produce approximately 72% of primary hydroxyl groups in end position with an OH number of 38.1,
 0.3 parts by weight of triethylenediamine,
 2.5 parts by weight of water and
 48 parts by weight of an isocyanate mixture consisting of 95% of an isocyanate which contains urethane groups and 5% of a mixture of urethane-containing and isocyanurate-containing 2,4- and 2,6-tolylene diisocyanate and 4,4'-diphenylmethane diisocyanate (NCO content 38.40%) are reacted together.

The isocyanate which contains urethane groups was prepared as given in Example 2-A.

The polyisocyanate which contains iso-

Density DIN 53420	(kg/m ³)	38
Tensile strength according to DIN 53571	(kg/wt/cm ²)	1.1
Elongation at break according to DIN 53571	(%)	160
Compression test DIN 53577	(p/cm ²)	30
Inflammability according to ASTM D 1692-67 T		
Average length of burnt sample	(cm)	40
Average extinction time	(sec)	27
Assessment		self-extinguishing

Example 6

The following components are introduced into the mixing chamber of a foaming machine:

100 Parts by weight of a polypropylene glycol which has been initiated on trimethylolpropane and tipped with ethylene oxide to produce approximately 72% of primary hydroxyl groups in end positions with an OH number of 38.1,
 0.2 parts by weight of triethylenediamine,
 0.2 parts by weight of N,N',N'' - penta-methyl - diethylene triamine,
 2.5 parts by weight of water,
 2.0 parts by weight of butane - 1,4 - diol and

Density according to DIN 53520	39 kg/m ³
Tensile strength according to DIN 53571	1.0 kg wt/cm ²
Elongation at break according to DIN 53571	190%
Compression strength at 40% compression according to DIN 53577	26 p/cm ²
Inflammability test according to ASTM D 1692/67 T	
Average length of burnt sample (cm)	3.5
Average extinction time (sec)	25

The foam resin is therefore to be regarded as self-extinguishing.

cyanurate groups was prepared as follows:

20 parts of 1,2-propylene glycol are added to a mixture of 225 parts of an 80/20 mixture of 2,4- and 2,6-tolylene diisocyanate and 275 parts of 4,4'-diphenylmethanediisocyanate at 60°C and the reactants are reacted together for 30 minutes. After the addition of 1 part of β -phenylethylethyleneimine, the reaction mixture is heated to 130°C. The trimerisation which takes place at this temperature is stopped after 2½ hours, when the NCO content of the reaction mixture is 26.5%, by the addition of 1 part of methyl p-toluenesulphonate. After dilution with 624 parts of an 80/82 mixture of 2,4- and 2,6-tolylene diisocyanate a polyisocyanate which has the following properties is obtained:

% NCO=38.4, cP_{25deg.}=24, n_D²⁰=1.5738.

A foam resin which has the following mechanical properties is obtained:

34.5 parts by weight of an isocyanate mixture consisting of 93% by weight of tolylene diisocyanate (80% of 2,4- and 20% of 2,4-isomer), 2% by weight of 2,4-tolylene diisocyanate which contains isocyanurate groups (NCO content 21.1%) and 5% by weight of an isocyanate which contains urethane groups (NCO content 35.8%, viscosity 77.8 cP at 25°C) and which has been obtained by reacting propoxylated trimethylolpropane (OH number 875) with tolylene diisocyanate (80% 2,4- and 20% 2,6-isomer) at 80 to 100°C.

A highly elastic foam resin which has the following properties is obtained:

Example 7

- 100 Parts by weight of a polypropylene glycol which has been initiated on trimethylolpropane tipped with ethylene oxide to produce approximately 72% of primary hydroxyl groups in end positions with an OH number of 38.1;
 0.3 parts by weight of triethylenediamine,
 2.5 parts by weight of water,
 4.0 parts by weight of butane - 1,4 - diol and
 4.0 parts by weight of tris-(dipropylene-glycol)phosphite are mixed together and
 69.5 parts by weight of an isocyanate mixture consisting of 55% by weight of tolylene diisocyanate (80% 2,4- and 20% 2,4-isomer), 5% by weight of polymeric

2,4-tolylene diisocyanate which contains isocyanurate groups (NCO content 21.1%) and 40% of an isocyanate which contains urethane groups (NCO content 32.9%, viscosity 808 cP at 25°C) and which was obtained by reacting propoxylated glycerol (OH number 1100) with tolylene diisocyanate (80% 2,4- and 20% 2,6-isomer) at 80 to 100°C. are added to the mixture.

Foam formation begins after an induction period of 10 seconds and is completed after 90 seconds. A soft, highly elastic foam resin is obtained which has the following properties:

	Density according to DIN 53420	41 kg/m ³
35	Tensile strength according to DIN 53571	0.8 kg wt/cm ²
	Elongation at break according to DIN 53571	170%
	Compression strength at 40% compression according to DIN 53577	23 p/cm ²
40	Inflammability test according to ASTM D 1692/67 T	
	Average length of burnt sample (cm)	3.1
	Average extinction time (sec)	43

The foam resin is therefore to be regarded as self-extinguishing.

Example 8

- 100.0 Parts by weight of a polypropylene-glycol which has been initiated on propylene glycol and tipped with ethylene oxide to produce approximately 67% of primary hydroxyl groups in end positions with an OH number of 28.0,
 3.0 parts by weight of water,
 0.2 parts by weight of dimethylamino-ethanol and
 1.0 part by weight of triethylamine are mixed together and reacted with

57.7 parts by weight of an isocyanate mixture has an NCO content of 28.9% and consists of 18 parts by weight of an isocyanate-containing adduct (NCO content 31.7%) of tripropylene glycol and 2,4- and 2,6-tolylene diisocyanate of which 80.0% is 2,4-tolylene diisocyanate, and 20 parts by weight of a polymeric 2,4-tolylene diisocyanate which contains isocyanate groups (NCO content 21.1%).

A foam resin which has the following mechanical properties and flame resistance is obtained:

	Density according to DIN 53420	37 kg/m ³
70	Tensile strength according to DIN 53571	1.2 kg wt/cm ²
	Elongation at break according to DIN 53571	195%
	Compression strength at 40% compression according to DIN 53577	34 p/cm ²
75	Inflammability according to test ASTM D 1692/67 T	
	Average length of burnt sample (cm)	2.5
	Average extinction time (sec)	23
80	Assessment of the foam resin	self-extinguishing

Example 9

- 100.0 Parts by weight of a polypropylene glycol which has been initiated on propylene glycol and tipped with ethylene oxide to produce approximately 67% of

primary hydroxyl groups in end positions with an OH number of 28.0,
 3.0 parts by weight of water
 0.2 parts by weight of dimethylamino-ethanol and

1.0 part by weight of triethylamine are mixed together and reacted with

5 50.4 parts by weight of an isocyanate mixture which has an NCO content of 33.1% and which consists of 80.0 parts by weight of an isocyanate-containing adduct (NCO content 31.7%) of tripropylene glycol and 2,4- and 2,6-tolylene diisocyanate comprising 80% of 2,4-tolylene diisocyanate and of 20.0 parts by weight of a urethane-containing and isocyanurate-containing 2,4- and 2,6-tolylene diisocyanate (80:20, NCO content 38.50%) which was prepared as follows:

1.33 Parts of 1,2 - propylene glycol are added to 27.50 parts of an 80/20 mixture of 2,4- and 2,6-tolylene diisocyanate at 60°C, and after a reaction time of 30 minutes, dur-

ing which the reaction mixture heats up to 80°C, 0.044 part of β -phenylethylethyleneimine is added. Using nitrogen as protective gas, the reaction mixture is then heated to 130°C. and trimerisation is stopped after a reaction time of about 5 hours at this temperature by adding 0.042 parts of benzoyl chloride, the NCO value being then 25.8%. After dilution of the reaction mixture with 71.50 parts of a 65/35 mixture of 2,4- and 2,6-tolylene diisocyanate, 5.28 parts of 2,3-dibromopropanol are added to this solution and the solution is then reacted for 2 hours at 80 to 90°C. The modified polyisocyanate solution has the following properties:

% NCO=38.5, $cP_{25deg.}=26$, $n_D^{20}=1.5690$.

A foam resin which has the following mechanical properties is obtained:

	Density DIN 53420	(kg/m ³)	36
	Tensile strength according to DIN 53571	(kg wt/cm ²)	1.3
40	Elongation at break according to DIN 53571	(%)	200
	Compression test DIN 53577	(p/cm ²)	35
	Inflammability according to ASTM D 1692-67 T		
45	Average length of burnt sample	(cm)	4.0
	Average extinction time	(sec)	25
	Assessment		self-extinguishing

Example 10

50 100.0 Parts by weight of a polypropylene glycol which has been initiated on propylene glycol and tipped with ethylene oxide to produce approximately 67% of primary hydroxyl groups in end positions with an OH number of 28.0,

55 3.0 parts by weight of water,
0.2 parts by weight of dimethylaminoethanol and
1.0 part by weight of triethylamine are mixed together and reacted with

60 50.4 parts by weight of an isocyanate mixture which has an NCO content of 33.10% and which consists of 80.0 parts by weight of an isocyanate-containing adduct (NCO content 31.7%) of tripropyleneglycol and 2,4- and 2,6-tolylene diisocyanate comprising 80% of 2,4-tolylene diisocyanate, and 20.0 parts by weight of a mixture of 2,4- and 2,6-tolylene diisocyanate which contains urethane groups and isocyanurate groups (80:20, NCO content 32.20%). The tolylene diisocyanate mixture which contains urethane groups and isocyanurate groups was prepared as follows:

0.40 Parts of a solution of water in acetone

(25 g of water made up to 1000 ml with acetone) and 0.038 parts of β -phenylethylethyleneimine are added to 25.00 parts of an 80/20 mixture of 2,4 and 2,6-tolylene diisocyanate at 22°C. The slightly exothermic trimerisation reaction of diisocyanate starts after a brief induction period and it is stopped after a reaction time of about 2 to 2½ hours, when the NCO content is 31.0% and the reaction temperature 70°C, by the addition of 0.204 parts by weight of methyl p-toluenesulphonate. With the reaction mixture at a temperature of 80°C, 3.00 parts by weight of tripropylene glycol are added and the reaction is left to proceed for 1½ hours at the same temperature. After the addition of 75 parts by weight of a mixture which consists of 2,4- and 2,6-tolylene diisocyanate in the ratio of 80:20% by weight and intensive homogenisation of the reactants, 5.42 parts by weight of 2,3-dibromopropanol are added at 90°C. After a reaction time of 2 hours at 90 to 100°C, the polyisocyanate combination has the following properties:

% NCO=38.2, $cP_{25deg.}=33.0$, $n_D^{20}=1.5790$.

A foam resin which has the following mechanical properties is obtained:

	Density DIN 53420	(kg/m ³)	36
	Tensile strength according to DIN 53571	(kg wt/cm ²)	1.1
5	Elongation at break according to DIN 53571	(%)	170
	Compression test DIN 53577	(p/cm ²)	40
	Inflammability according to ASTM D 1692-67 T		
10	Average length of burnt sample	(cm)	3.8
	Average extinction time	(sec)	31
	Assessment		self-extinguishing

Example 11

15	100.0 Parts by weight of a polypropylene glycol which has been initiated on propylene glycol and tipped with ethylene oxide to produce approximately 67% of primary hydroxyl groups in end positions with an OH number of 28.0,	has an NCO content of 26.2% and which consists of 79.5% by weight of an isocyanate containing adduct (NCO content 27.62%) of tripropylene glycol and 2,4- and 2,6- tolylene diisocyanate comprising 80% of 2,4-tolylene diisocyanate and 4,4' - diisocyanatodiphenylmethane in the ratio of 3:2 and 20.5 parts by weight of a polymeric 2,4-tolylene diisocyanate which contains isocyanurate groups (NCO content 21.1%).	30
20	3.0 parts by weight of water, 0.2 parts by weight of dimethylaminomethanol and 1.0 part by weight or triethylamine		35

and mixed together and reacted with

25	63.5 parts by weight of an isocyanate which	A foam resin which has the following mechanical properties and flame resistance is obtained:	
40	Density according to DIN 53420	40.0 kg/m ³	
	Tensile strength according to DIN 53571	1.1 kg wt/cm ²	
	Elongation at break according to DIN 53571	160%	
45	Compression strength at 40% compression according to DIN 53577	43 p/cm ²	
	Inflammability according to ASTM D 1692/67 T		
	Average extinction time	22 sec.	

Example 12

50	100.0 Parts by weight of a polypropylene glycol which has been initiated on propylene glycol and tipped with ethylene oxide to produce approximately 67% of primary hydroxyl groups in end positions with an OH number of 28,	in the ratio of 3:2 and 20.5 parts by weight of a 2,4-tolylene diisocyanate (NCO content 39.5%) which contains urethane groups and isocyanurate groups.	
55	3.0 parts by weight of water, 0.2 parts by weight of dimethylaminoethanol and 1.0 part by weight of triethylamine	The polyisocyanate which contains urethane groups and isocyanate groups was prepared as follows:	75
60	are mixed together and reacted with		
65	55.5 parts by weight of a polyisocyanate solution which has an NCO content of 30.2% and which consists of 79.5 parts by weight of an isocyanate-containing adduct (NCO content 27.62% of tripropylene glycol and a mixture of 2,4- and 2,6-tolylene diisocyanate containing 80% of 2,4-tolylene diisocyanate and 4,4'-diisocyanatodiphenyl methane	0.061 Parts by weight of a solution of water in acetone (25 g of water made up to 1000 ml with acetone) and 0.058 parts by weight of β - phenylethyl - ethyleneimine are added to 38.76 parts by weight of tolylene - 2,4 - diisocyanate at 25°C. The slightly exothermic trimerisation reaction of diisocyanate starts after a brief induction period. It is stopped after about 2 hours, at an NCO content of 31.0 to 31.3%, by the addition of 0.042 parts by weight of benzoyl chloride. The reaction mixture is then heated to 80°C and 2.33 parts by weight of tripropylene glycol are added in the course of 10 to	80
70			85
			90

minutes, the reaction mixture reaching a temperature of 95 to 100°C. Stirring is then continued for one hour without any further supply of heat and the reaction mixture is then diluted with 58.91 parts by weight of an 80/20 mixture of 2,4- and 2,6-tolylene diisocyanate. The solution of the modified

isocyanurate polyisocyanate in tolylene diisocyanate has the following properties:

% NCO=39.5, $cP_{25deg.}=54$, $n_D^{20}=1.5827$. 10

A foam resin which has the following mechanical properties is obtained:

15	Density DIN 53420	(kg/m ³)	40
	Tensile strength according to DIN 53571	(kg wt/cm ²)	1.1
	Elongation at break according to DIN 53571	(%)	160
	Compression test DIN 53577	(p/cm ²)	40
20	Inflammability according to ASTM D 1692—67 T		
	Average length of burnt sample	(cm)	2.3
	Average extinction time	(sec)	22
	Assessment		self-extinguishing

Example 13

25 100.0 Parts by weight of a polypropylene glycol which has been initiated on propylene glycol and tipped with ethylene oxide to produce approximately 67% of primary hydroxyl groups in end positions with an OH number of 28,
30 3.0 parts by weight of water
0.2 parts by weight of dimethylamino-ethanol and
1.0 part by weight of triethylamine

35 are mixed together and reacted with

56.50 parts by weight of a polyisocyanate solution which has an NCO content of 29.4% and which consists of 79.5 parts by weight of an isocyanate-containing adduct (NCO content 27.62%) of tripropylene glycol and a mixture of 2,4- and 2,6-tolylene diisocyanate containing

80% of 2,4-tolylene diisocyanate and 4,4'-diisocyanatodiphenylmethane in the ratio of 3:2 and 20.5 parts by weight of a polymeric 2,4-tolylene diisocyanate which contains isocyanurate groups (NCO content 36.0%) which was prepared as follows: 45

5 Parts by weight of 2,3-dibromopropanol are added to 95 parts by weight of the modified isocyanurate polyisocyanate described in Example 12 in tolylene diisocyanate at 90°C and the components are reacted at this temperature for 2 hours. The resulting polyisocyanate solution has the following properties: 50 55

% NCO=36.0, $cP_{25deg.}=81$, $n_D^{20}=1.5858$.

A foam resin which has the following mechanical properties is obtained:

60	Density DIN 53420	(kg/m ³)	39
	Tensile strength according to DIN 53571	(kg wt/cm ²)	0.9
	Elongation at break according to DIN 53571	(%)	160
	Compression test DIN 53577	(p/cm ²)	30
65	Inflammability according to ASTM D 1692—67 T		
	Average length of burnt sample	(cm)	2.8
	Average extinction time	(sec)	15
	Assessment		self-extinguishing

WHAT WE CLAIM IS:—

1. A process for the production of a polyurethane foam which comprises reacting:—

75 (a) at least one polyether which contains at least two reactive hydrogen atoms and has a molecular weight of 1,500 to 10,000 and in which at least 10% of the hydroxyl groups are primary hydroxyl groups,

(b) at least one polyisocyanate solution which is a 1 to 80% solution by weight of at least one polyisocyanate which comprises at least one isocyanurate ring dissolved in at least one polyisocyanate which is free from isocyanurate groups but which comprises urethane groups, 80 85
(c) a blowing agent.

2. A process as claimed in Claim 1 in

which component (b) is a 5 to 60% by weight solution.

3. A process as claimed in Claim 1 or Claim 2 in which the said polyisocyanate
5 which comprises isocyanurate groups also comprises urethane groups.

4. A process as claimed in any of Claims 1 to 3 in which component (b) also comprises one or more monomeric isocyanates
10 which are free from both isocyanurate and urethane groups.

5. A process as claimed in Claim 1 sub-

stantially as herein described with reference to any one of the Examples.

6. Foam resins when produced by a process as claimed in any of Claims 1 to 5. 15

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